How to Cite: Glukhikh, V.V., Shkuro, A.E., & Krivonogov, P.S. (2021) The effect of chemical composition on the biodegradation rate and physical and mechanical properties of polymer composites with lignocellulose fillers. *Bulletin of the University of Karaganda – Chemistry*, *103*(*3*), 83-92. https://doi.org/10.31489/2021Ch3/83-92

UDC 674.81

https://doi.org/10.31489/2021Ch3/83-92

V.V. Glukhikh*, A.E. Shkuro, P.S. Krivonogov

Ural State Forest Engineering University, Yekaterinburg, Russia (*Corresponding author's e-mail: gluhihvv@m.usfeu.ru)

The effect of chemical composition on the biodegradation rate and physical and mechanical properties of polymer composites with lignocellulose fillers

The results of TPLC scientific research, practical experience of their preparation, and application as of 2016 are presented in eight volumes of the "Handbook of Composites from Renewable Materials" (2017, John Wiley & Sons, Inc.). This article provides an analysis of books and articles with open access to the Science Direct (Elsevier) database for the period 2017–2020 to assess the biodegradation rate and physical and mechanical properties of polymer composites with lignocellulosic fillers. The production and use of polymer composites with a thermoplastic polymer matrix and lignocellulosic fillers (TPLC) have significant ecological and economic prospects since waste biomass from forests, agriculture, and polymers obtained from petroleum raw materials can be used for their production. However, depending on the TPLC application area, there are opposite requirements for the biodegradation rate. For the use in construction and medicine materials and products must have a minimum biodegradation rate. Materials and products for single-use packaging must have the necessary biodegradability potential and have an adjusted biodegradation rate in soil, water, compost environment. Research results show that the properties of TPLC can be significantly influenced not only by the physical but also by the chemical structure of all components of these composites. The chemical properties of polymers, fillers, additives for various purposes can affect their industrial production efficiency.

Keywords: composite, chemical structure, thermoplastic polymer, filler, cellulose, lignin, biodegradation, properties.

Introduction

To date there is no conventional terminology in the scientific literature to designate composites based on rapidly renewable raw materials. These composites are ordinarily termed "biocomposites", "green composites", "bioplastics". Composite materials obtained from recycled synthetic polymers with plant-based fillers began to be called "eco-composites" [1].

Lignocellulosic-filled composites are an enormous group of materials that include composites with an organic and inorganic binder phase. CMLC with binders based on thermoplastic polymers finds a wide and varied practical application. Composites with a thermoplastic polymer phase and lignocellulose fillers (TPLC) are used in significant volumes in the automotive industry, furniture, and construction materials. The results of the TPLC scientific research, practical experience and application as of 2016 are presented in eight volumes of "Handbook of Composites from Renewable Materials" (2017, John Wiley & Sons, Inc.).

According to scientific materials published in journals and books in 2017–2020 and the first half of 2021 [2–4], an increase in commercial interest in the production of TPLC and their use in medicine, water treatment, heat power engineering, packaging, aerospace industry, automotive structural parts, building materials, furniture, and driveways is predicted. At the same time there is also an environmental interest, as waste thermoplastic polymers (polyethylene, polypropylene) may be used to produce TPLC. TPLC products may be recycled after use as well. The chemical sciences play an essential role in the processing of various wastes, including not only polymeric materials [5] but also the residues of forest biomass [6] and agriculture [7] due to their use for the production of popular marketable products from TPLC.

Until now, the priority goal of scientific TPLC research is to study the influence of their components' morphological, physical, and chemical parameters on the physicomechanical and functional properties. However, the studies of the TPLC component's chemical composition influence their biodegradation rate have not been systemic and are difficult to meta-analysis since a great variety of methods for its assessment.

Depending on the area of application of TPLC there are opposite requirements for the rate of their biodegradation. For example, construction materials and products that directly contact soil, water, microorganisms, and solar radiation must have a minimum biodegradation rate. The medical industry also needs bioresistant products. On the other hand, materials and products for single-use packaging must have the necessary biodegradability potential and have a given biodegradation rate in soil, water, and compost environment. Currently, in connection with the tightening of requirements for the environmental safety of consumer waste in several countries, there is a need for TPLC products with a given biodegradation rate and the change dynamics of physical and mechanical properties.

Many countries enacted laws prohibiting the production of non-biodegradable plastics for reducing plastic waste. Thanks to this, scientific research of biodegradable TPLC is actively developing. The activity in conducting scientific research on the production and study of biostable TPLC is low. There is an erroneous opinion [2, 3] that TPLC with a synthetic polymer matrix has a very high biostability. Rapid laboratory test results often form this opinion. A.A. Klyosov [8] noted that ASTM standard microbial resistance tests generally showed that TPLCs have excellent microbial resistance properties. However, in his opinion, laboratory results and environmental impacts do not always correlate.

Recent studies [9–12] have confirmed the biodegradability of TPLC materials. Biodegradation of TPLC occurred primarily due to the action on lignocellulose fillers (LCP) in the composite of various rotting and mold fungi, algae, and termites.

In the study [10] an express assessment of the biodegradation potential in active soil of various TPLC products obtained by multiple methods was carried out. The authors assessed biodegradation by the dynamics of changes in their morphological and visual characteristics. They used five types of soil substrates with different compositions of microbiocenosis. The maximum exposure time of the samples in soil substrates was at least nine months. At the same time, to analyze the potential phytotoxicity of TPLC biodegradation products, a test with growing annual plants in soil substrates was carried out. The research results showed that all tested TPLC products have a higher biodegradability potential in soil than polyethylene, polypropylene, and polyethylene terephthalate. In addition, the breakdown of the lignocellulosic filler gave the polymer composites a characteristic spongy appearance by "emptying" the polymer matrix (Fig. 1).

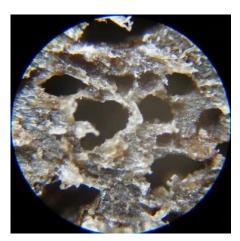


Figure 1. A sample of a strand obtained by extrusion from a mixture of polyethylene and wheat husk after holding in an active soil for nine months (\times 160 magnification)

A.A. Klyosov gave the factors influencing the TPLC biodegradation rate in the book [8]. According to him and the results of many recent studies [11, 12], moisture content (absorption) is one of the critical parameters for the growth of microorganisms in TPLC materials. However, there is a strong correlation between the total moisture content of the TPLC and its susceptibility to microbial degradation.

As noted by the authors of many recent studies, in addition to the moisture content the following physicochemical parameters of the composites also significantly affect the physical and mechanical properties and the TPLC biodegradation rate under the influence of various microorganisms:

- Physicochemical structure and composition of the polymer phase;
- Content and chemical structure of lignin and cellulose in fillers;
- Content and chemical structure of special additives (biocides, plasticizers, and others).

Influence of the polymer phase physicochemical structure and composition on the TPLC properties and biodegradation rate

Until now the names of polymers used in publications have often not matched with their chemical structure. For example, a polymer synthesized by polymerization reactions of ethylene obtained by a microbiological method is called "bio polyethylene" and belongs to the group of biopolymers. The name "microbiological cellulose" appears similarly. In this article we use polymers' words corresponding to their chemical composition rather than the origin of the monomers for their synthesis. Natural polymers are obtained from natural raw materials, and synthetic polymers are obtained by industrial synthesis from monomers. The term "bio-polymers" combines natural polymers and synthetic polymers of a similar chemical composition obtained from monomers of natural origin.

Based on many research results in the review [13], the authors proposed to divide biodegradable polymers into three groups: unmodified biopolymers, structurally modified biopolymers, and chemically modified biopolymers. Review authors concluded that the structural modification has practically no effect on its biodegradation in soil, and chemically modified biopolymers can be subjected to different biodegradation mechanisms and, consequently, have different rates of biodegradation. In many cases, biodegradable plastics made from biopolymers retained the regularities of biodegradation in soil, characteristic of biopolymers. These conclusions followed the example of thermoplastic starch, cellulose acetate, and lignin. When the chemical structure of the polymer changes, as in the case of cellulose acetate, various microorganisms and enzymes were involved in biodegradation. Based on the biodegradation process of cellulose acetate, the authors of the review proposed a conceptual model that can be used as a starting point for predicting biodegradation, the rate of decomposition of other chemically modified biopolymers used as bioplastics. This review noted that cellulose, like starch, is a glucose polysaccharide, but cellulose is more resistant to biodegradation because it contains prepotent β -glycosidic bonds. The degree of cellulose crystallinity affected the rate of biodegradation in soil. The biodegradation of amorphous cellulose was faster than the biodegradation of crystalline cellulose. Acetylation of cellulose slowed down its biodegradation rate, i.e., the acetyl groups protected against microbial attack. The degradation rate depended on the degree of cellulose acetylation, the distribution of acetyl groups along the cellulose chain, and its molecular weight. The results of studies that have established a negative nonlinear dependence of the rate of enzymatic decomposition of films based on cellulose on the degree of its acetylation are cited.

The review [14] drawn attention to the industrial production of composites with a polymer matrix from two or more polymers mixtures, and due to this, proposed a viable alternative for reducing the cost of industrial products. These blends in various combinations have been used to produce traditional and biodegradable plastics to improve some of their mechanical properties, regulate product life cycles and reduce manufacturing costs.

Currently, the most prominent polymer matrix for producing biodegradable composites is polylactide (PLA). Its availability has significantly increased in the past decade, and its prices have dropped. That was making polylactide a competitive material. The polylactide biodegradation process has been well studied not only in tests but also in practical terms. The fundamental limitations that prevent the use of pure PLA are its fragility and toughness. However, this problem can be solved by mixing PLA with other bio-based polymers, including thermoplastic starch (TPS), polyhydroxybutyrate valerate (PHBV), which allows the use of composites with a polymer matrix from these mixtures in almost any conditions. The example of PLA, which is increasingly used in commercial solutions, demonstrates the necessity to continue large-scale research on the use of its mixtures with other polymers, for example, polyhydroxyalkanoates (PHB) polybutylene succinate (PBS), modified starch, modified polyethylene terephthalate (PET). The biodegradation of composites with such mixtures under practical terms has not been sufficiently studied. Synthetic polymers containing fragments that accelerate the biodegradability process can be used to make composites biodegradable. These can be polyesters and polyesteramides, copolyesters based on aliphatic diols, and organic dicarboxylic acids. Unfortunately, this work does not provide a comparative assessment of the effect of the type and amount of functional groups introduced into the structure of synthetic polymers on the rate of TPLC biodegradation. The method of producing biodegradable polymeric materials consists in obtaining composites based on natural polymers: starch, cellulose, chitosan, proteins. However, a comparative assessment of various factors' effect on the biodegradation rate is given only for polymers. Data on the performance properties of composites during their biodegradation are not provided.

Considering the possible prospects for the industrial production of TPLC products, scientific research continues to study the properties of composites with synthetic biodegradable polymer matrices, mixtures of biopolymers with synthetic biodegradable polymers with chemical modification of these polymers and additives.

The review [12] presented a detailed analysis of the effect of the physicochemical structure and composition of the polymer phase consisting of some synthetic polyolefins and their mixtures (polyethylene, polypropylene and their mixtures, propylene-ethylene copolymers, ethylene-vinyl acetate, ethylene-octene, and their combinations), on the biodegradation of TPLC. In these composites, cellulose and wood flour were used as fillers with a content of 0 to 30 %. This work analyzed the influence of the following factors on the composites biodegradable properties:

- chemical structure and conformation of monomeric units and branching of the macromolecular chain;
- chemical composition of copolymers of ethylene with propylene, ethylene with vinyl acetate, ethylene with octene;
- regularity of distribution of ethylene units in copolymers with propylene;
- supramolecular structure of polymers, including the degree of crystallinity and orientation effect;
- phase structure of polymer blends of polyolefins. The authors made conclusions about the influence of these factors on the processes of rupture of polymer macromolecules, water absorption of composites, and their assimilation by microorganisms by the following mechanisms:
- chemical structure of polymer monomer units;
- the presence of hydrolyzable functional groups in the polymer backbone;
- conformation and branching of the main macromolecular chain;
- type of distribution of monomer units in the copolymer.

This work did not provide information on the effect of the polymer physicochemical structure on the properties of the composites during biodegradation.

Biodegradation studies of composites with synthetic and natural polymers associated with assessing their functional properties are ongoing. At the same time, methods are being developed for obtaining new composites not only with above mentioned synthetic, natural polymers and their mixtures but also with others. However, based on the results of these studies, it is impossible to draw general conclusions about the effect of the polymer phase physicochemical structure and composition on the TPLC biodegradation rate since the studied composites did not have an accurate same chemical composition.

Influence of the content and chemical structure of lignin and cellulose in fillers on the TPLC properties and biodegradation rate

The origin of the natural lignocellulosic filler usually determines its chemical composition and structure. However, these fillers contain cellulose, lignin, hemicelluloses, extracts, and other substances regardless of genesis. There are no doubts about the conclusions based on the results of the studies performed on a higher rate of TPLC biodegradation with a decrease in the lignin content in the cell walls of lignocellulose fillers. Therefore, in many studies, the content of cellulose and lignin in LCPs is controlled. In addition, new data have appeared on the effect of the fiber content in the filler on the TPLC properties [1], which, in addition to cellulose and lignin, may contain other chemical substances.

The review [2] presented a comprehensive analysis of the components and their features and many other factors that influence the mechanical properties and prospects for the composites with a biopolymer matrix. The physicochemical structure of the polymer matrix, fillers, plasticizers, and other biocomposites components significantly affected the properties of such composites. A significant aspect for obtaining composites with desired properties was searching for optimal parameters for their preparation: homogeneous distribution of components in the polymer matrix, the optimal amount of filler, and the optimal interfacial connection of elements. Biocomposite's mechanical properties could be adjusted by choosing an appropriate biopolymer. Adaptation of functional groups to potent compounds due to their physical and chemical modifications improved interfacial bonding. The work [15] provided data on all-cellulosic composites (ACC) properties with a cellulosic polymer matrix and cellulosic fillers. Films made of these composites had high physical and mechanical properties, as well as light transmission. In terms of their mechanical properties, these materials were superior to most commercial composites with nano cellulosic fillers and other polymer matrices due to the ideal bonding of the cellulosic filler to the cellulosic matrix because of their identical chemical composition. Furthermore, experiments on the burial of composites in soil have shown that ACC biodegradability is better than other biodegradable polymers such as polylactic acid. In this case, the biodegradation of ACC occurred mainly in the matrix phase.

The authors of the review [14] classed lignin as an amorphous polyester heteropolymer with aromatic alcohol groups. Lignin is a more rot-resistant polymer than starch and cellulose due to its complex chemical structure. Therefore, the lignin biodegradation rate in the composition of lignocellulose complexes was lower than that of free lignin obtained in the pulp and paper industry. Consequently, many physical and mechanical

properties of composites with a polymer matrix of lignin and starch were inferior to those of composites with a cellulose matrix.

Recently, studies of the effect of various fillers, including cellulose and lignin, isolated from plant materials, various plant wastes, and products of their chemical modification on the biodegradability and other TPLC properties have intensified [1, 14, 16-21].

The review [16] analyzed the studies of composites with a polyurethane polymer phase and fillers obtained by functionalizing lignin with various chemical compounds. The use of lignin chemical modification products significantly improved the mechanical properties of polyurethane composites compared to unmodified lignin. Therefore, the review authors believe that its use as a filler for thermoplastic polyurethanes has an industrial perspective.

The review [17] analyzed the studies of lignin nanoparticles and products of their chemical modification as fillers for various thermoplastic polymers. During the chemical modification of nano lignin by different reactions new functional groups are formed (functionalization) on the surface of lignin nanoparticles. According to the conclusions of the review authors, functionalized nano lignin in composites with different polymer phases retained the antimicrobial properties inherent in ordinary lignin. Improvement of the performance properties of composites with varying phases of a polymer depends on the type and content of functional groups in nano lignin, depending on the chemical structure of the polymer. According to the reviewers, nano lignin is an ideal material with a promising future in nanocomposites.

The authors of the article [18], based on the results of their research on composites with a polymeric phase of polylactic acid and a filler based on cellulose waste fibers, noted that chemical modification of the filler with lactic acid improves the biodegradability of the composite and some of its mechanical properties.

The authors of [19] described the chemical interaction of two silanes with surface functional groups of lignocellulose particles and the chemical bond between them. The authors suggested that functionalization of the lignocellulose surface leads to stronger bonds in the composite between the LCP and the polymer matrix of the ethylene-norbornene copolymer. Furthermore, the modification of lignocellulose by silanes increased the thermal stability of these composites, and the effect on the elastic modulus of the composites is the opposite: N-(2-aminoethyl)-3-aminopropyltrimethoxysilane decreases this index, while vinyltrimethoxysilane increases. Thus, in future studies the authors hoped to obtain epy evidence of an increase in the hydrophobic properties of composites with lignocellulosic fillers with a silane-modified surface.

The authors of the article [20] investigated the preliminary treatment of bagasse powder with choline acetate to improve the properties of polypropylene composites. The results showed a positive effect of filler functionalization on the tensile strength of the composite and a decrease in its porosity by increasing the compatibility of the polypropylene phase with the filler treated with choline acetate.

In [21] the influence of aspen sawdust treatment with a water-soluble polyelectrolyte complex (LPEC), consisting of hardwood soda lignin and polyethyleneimine on the properties of a wood-polymer composite (WPC) with recycled polypropylene were established. The treatment of sawdust with LPEC nanoparticles increased the content of fixed nitrogen in them and led to a slight improvement in the mechanical properties of WPC and a decrease in their wettability. Furthermore, the authors explained the revealed effect of a reduction in the ability of WPC to be wetted with water because of the imine and amide bonds formed between the free amino groups of LPEC and the carbonyl and carboxyl groups of the lignocellulose matrix of the modified topics.

In general, it can be considered that the results of recent studies confirmed not only a significant effect on the TPLC properties of cellulose and lignin content in fillers but also the prospects of regulating this effect using a chemical modification of lignocellulosic fillers by various methods. However, systematic studies of the impact on TPLC properties of the content of hemicelluloses and extractives in lignocellulosic fillers were not carried out.

Influence of content and chemical structure of special additives on TPLC properties and biodegradation rate

For the production of TPLC products various chemicals are used as special purpose additives. For example, biocides (antiseptics) are added to the TPLC to increase biostability. In addition, depending on the manufacturing technology of TPLC products, the composite contains plasticizers, compatibilizers, lubricants, and other additives [8]. There is no doubt that some of these additives can affect the chemical structure of the surfaces of the polymer and filler phases in TPLC, the processes of physicochemical interactions between phases, and change the structure and properties of composites.

With the wide variety of environmental parameters leading to TPLC biodegradation, to decrease the rate of composites biodegradation (increase their biostability) modern scientific research continues mainly to find effective biocides for specific operating conditions of products made from these composite materials. At the same time, the search for biocides is carried out among inorganic compounds of various metals, organic compounds of different chemical structures, and the origins of their mixtures. Therefore, nanobiocides are of great interest to scientists [2].

Many factors, including the chemical structure of TPLC components, affect the effectiveness of biocides. For example, the article [9] reported that for composites with a polyethylene matrix and lignocellulosic fillers (flour from wood and bamboo), the composition and chemical structure of the extractive substances of the fillers affect the effectiveness of biocides. The biocides used were 4,5-dichloro-2-octithiazolone, zinc pyrithione, and carbendazim. The extractive matters of the fillers in the presence of biocides had a positive or negative effect on the resistance to algal and fungal degradation of TPLC.

Chinese scientists continued their studies [22] to assess the effect on the properties of TPLC of organomontmorillonite (OMMT) additives synthesized in situ by the exchange of montmorillonite sodium cations for dodecyl dimethyl ammonium chloride. Composites were prepared by hot pressing from mixtures of polypropylene (PP), lignocellulose flour, and OMMT obtained in a twin-screw extruder. The mass ratio of lignocellulose flour/PP was 1:1. Three types of lignocellulose flour were used: poplar flour (WF), cellulose flour (CF), and lignin flour (LF). Studies results showed that the OMMT conferred on TPLC with a polypropylene matrix and lignocellulose flour against fungi of brown (Gloeophyllum trabeum) and white (Coriolus Versicolor) rot. The TPLC mass loss after exposure to rot-fungi for 12 weeks ranged from 0 to 6 %, in contrast to solid pine and poplar wood (over 45 %). The TPLC resistance to brown and white rot varied and depended on the type of lignocellulosic filler.

The review [22] assessed the state and prospects of obtaining antimicrobial composite materials for active packaging of food products, which contain antibacterial nanoparticles (metals, metal oxides, mesoporous silica, and graphene-based nanomaterials) with biodegradable polymers (gelatin, alginate, cellulose, and chitosan).

The state and prospects of using oxo-biodegradable additives to obtain TPLC based on synthetic polymers with increased resistance to UV radiation and microorganisms are reviewed [23].

The general regularities of the influence of special additives chemical structure on TPLC biodegradation rate have not been revealed. TPLC production forecasts, considering their environmental friendliness and economic feasibility, are presented in reviews [1, 24, 25].

Conclusions

The production and use of composites with a thermoplastic polymer matrix and lignocellulosic fillers (TPLC) have environmental and economic prospects since waste biomass from forests, agriculture, and plastics is obtained from raw petroleum materials be used for their production. The results of recent studies have confirmed and, in some cases, established the influence of the chemical composition of the polymer phase and lignocellulosic fillers of composites on the performance properties of products obtained from TPLC. This influence on TPLC's physical and mechanical properties and, to a lesser extent, on the rate of their biodegradation in various media has been studied in more detail. Furthermore, TPLC's biodegradability rate is associated with various microorganisms and bacteria used in research and their composition and technological modes of preparation.

The overall conclusion of recent studies is experimental confirmation of a significant effect of TPLC's ability to absorb water and its vapor on their biodegradation rate. The authors of several studies [26–30] predicted the biodegradation rate based on water absorption or sorption by the composites. Another conclusion is that the TPLC biodegradation rate rises with increasing lignocellulose content while its chemical composition remains constant.

The influence of thermoplastic synthetic polymers' physicochemical structure on the TPLC biodegradation rate is explained by the presence of functional groups in the polymer phase that affect its degree of crystallinity, interaction with functional groups of the lignocellulosic filler, uniform distribution of filler particles, and their agglomeration in the composite. However, assessing the effect of the natural polymers' physicochemical structure and the presence and amount of functional groups in the polymer phase on TPLC biodegradation rate is still uncertain.

There is no doubt only the previously established regularity of decrease in TPLC biodegradation rate with an increase in the polymer phase composites deacetylation degree based on cellulose acetate [31].

The modern assessment of TPLC biodegradation rate from the physicochemical structure of lignocellulosic fillers requires simultaneous consideration of their particle size and morphology, which significantly affect the water absorption of composites. Recent studies have confirmed a significant impact on the TPLC biodegradation rate of cellulose and lignin content in fillers and the promise of regulating this effect using a chemical modification of lignocellulose fillers. However, one should consider that the range of plant fillers in which the content of not cellulose and lignin, but other compounds predominates is expanding.

Research on reducing the TPLC biodegradation rate due to the introduction of biocides into their composition continues, but unfortunately, in modern research the environmental hazard of degradation products in soil and water is not assessed.

References

1 Nassar M.M.A. Progress and challenges in sustainability, compatibility, and production of eco-composites: A state-of-art review / M.M.A. Nassar, K.I. Alzebdeh, T. Pervez, N. Al-Hinai, A. Munam // J. Appl. Polym. Sci. — 2021. — P. 51284. https://doi.org/10.1002/app.51284.

2 Vinod A. Review. Renewable and sustainable biobased materials: An assessment on biofibers, biofilms, biopolymers and biocomposites / A. Vinod, M.R. Sanjay, S. Suchart, P. Jyotishkumar // Journal of Cleaner Production. — 2020. — Vol. 258. — P. 1–27. https://doi.org/10.1016/j.jclepro.2020.120978.

3 Rodriguez L.J. A literature review on life cycle tools fostering holistic sustainability assessment: An application in biocomposite materials / L.J. Rodriguez, P. Peças, H. Carvalho, C.E. Orrego // Journal of Environmental Management. — 2020. — Vol. 262. — P. 110308. https://doi.org/10.1016/j.jenvman.2020.110308.

4 Feng J. Effects of fungal decay on properties of mechanical, chemical, and water absorption of wood plastic composites / J. Feng, S. Li, R. Peng, T. Sun, X. Xie, Q. Shi // J. Appl. Polym. Sci. — 2020. — P. 50022. https://doi.org/10.1002/app.50022.

5 Matlin S.A. Material circularity and the role of the chemical sciences as a key enabler of a sustainable post-trash age / S.A. Matlin, G. Mehta, H. Hopf, A. Krief, L. Keßlerf, K. Kümmerer // Sustainable Chemistry and Pharmacy. — 2020. — Vol. 17. — P. 100312. https://doi.org/10.1016/j.scp.2020.100312.

6 Braghiroli F.L. Valorization of Biomass Residues from Forest Operations and Wood Manufacturing Presents a Wide Range of Sustainable and Innovative Possibilities / F.L. Braghiroli, L. Passarini // Current Forestry Reports. — 2020. — Vol. 6. — P. 172–183. https://doi.org/10.1007/s40725-020-00112-9.

7 Tajeddin B. The effect of wheat straw bleaching on some mechanical properties of wheat straw/LDPE biocomposites / B. Tajeddin, R.F. Momen // Journal of Food and Bioprocess Engineering. — 2020. — Vol. 3, No. 1 — P. 23–28. https://doi.org/10.0.86.43/JFABE.2020.75620.

8 Клёсов А.А. Древесно-полимерные композиты / А.А. Клёсов. — СПб.: Научные основы и технологии, 2010. — С. 461–512.

9 Feng J. Effects of biocide treatments on durability of wood and bamboo/high density polyethylene composites against algal and fungal decay / J. Feng, J. Chen, M. Chen, X. Su, Q. Shi // J. Appl. Polym. Sci. — 2017. — P. 45148. DOI: 10.1002/APP.45148.

10 Glukhikh V.V. Plastics: physical-and-mechanical properties and biodegradable potential / V.V. Glukhikh, V.G. Buryndin, A.V. Artemov, A.V. Savinovskih, P.S. Krivonogov, A.S. Krivonogova // Foods and Raw Material. — 2020. — Vol. 8, No 1. — P. 149–154. https://doi.org/10.21603/2308-4057-2020-1-149-154.

11 Candelier K. Termite and decay resistance of bioplast-spruce green wood-plastic composites / K. Candelier, A. Atli, J. Alteyrac // European Journal of Wood and Wood Products. — 2019. — Vol. 77. — P. 157–169. https://doi.org/10.1007/s00107-018-1368-y.

12 Попов А.А. Биоразлагаемые композиционные материалы. (Обзор) / А.А. Попов, А.К. Зыкова, Е.Е. Масталыгина // Химическая физика. — 2020. — Т. 39, № 6. — С. 71–80.

13 Polman E.M.N. Comparison of the aerobic biodegradation of biopolymers and the corresponding bio-plastics: A review / E.M.N. Polman, G.-J.M. Gruter, J.R. Parsons, A. Tietema // Science of the Total Environment. — 2021. — Vol. 753. — P. 141953. https://doi.org/10.1016/j.scitotenv.2020.141953 0048-9697.

14 Marczak D. Characteristics of biodegradable textiles used in environmental engineering: A comprehensive review / D. Marczak, K. Lejcus, J. Misiewicz // Journal of Cleaner Production. — 2020. — Vol. 268. — P. 122129. https://doi.org/10.1016/j.jcle-pro.2020.122129.

15 Fujisawa S. All-Cellulose (Cellulose–Cellulose) Green Composites / S. Fujisawa, T. Saito, and A. Isogai // Advanced Green Composites. — 2018. — P. 111–134. https://doi.org/10.1002/9781119323327.

16 Li H. Conversion of biomass lignin to high-value polyurethane: A review / H. Li, Y. Lianga, P. Li, C. He // Journal of Bioresources and Bioproducts. — 2020. — Vol. 5, No 3. — P. 163–179.

17 Parvathy, G. Lignin based nano-composites: Synthesis and applications / G. Parvathy, S. AS, J. S Jayan, A. Raman, A. Saritha // Process Safety and Environmental Protection. — 2021. — Vol. 145. — P. 395–410. https://doi.org/10.1016/j.psep.2020.11.017 0957-5820.

18 Gama N. New poly(lactic acid) composites produced from coffee beverage wastes // N. Gama, A. Ferreira, D.V. Evtuguin // J. Appl. Polym. Sci. — 2021. — Vol. 138, No. 35. — P. 51434. https://doi.org/10.1002/app.51434.

19 Wolski K. Surface hydrophobisation of lignocellulosic waste for the preparation of biothermoelastoplastic composites / K. Wolski, S. Cichosz, A. Masek // European Polymer Journal. — 2019. — Vol. 118. — P. 481–491.

20 Ninomiya K. Ionic liquid pretreatment of bagasse improves mechanical property of bagasse/polypropylene composites / K. Ninomiya, M. Abe, T. Tsukegi, K. Kuroda, M. Omichi, K. Takada, et al. // Industrial Crops & Products — 2017. — Vol. 109. — P. 158–162. http://dx.doi.Org/10.1016/j.indcrop.2017.08.019.

21 Shulga G. Lignin-containing Adhesion Enhancer for Wood-plastic Composites / G. Shulga, B. Neiberte, J. Jaunslavietis, A. Verovkins, S. Vitolina, V. Shakels, et al. // BioResources. — 2021. — Vol. 16, No. 2. — P. 2804–2823. https://doi.org/10.15376/biores.16.2.2804-2823.

22 Liu R. Fungi Resistance of Organo-Montmorillonite Modified Lignocellulosic Flour/Polypropylene Composites // R. Liu, M. Liu, J. Cao, E. Ma, A. Huang // POLYMER COMPOSITES-2017. — 2017. https://doi.org/10.1002/pc.24413.

23 Луканина Ю.К. Оксо-биодеградируемые полимерные материалы. (Обзор) / Ю.К. Луканина, А.А. Попов // Все материалы. Энцикл. справ. — 2021 — № 3. — С. 9–15. https://doi.org/10.31044/1994-6260-2021-0-3-9-15.

24 Vikhareva I.N. An Overview of the Main Trends in the Creation of Biodegradable Polymer Materials /I.N. Vikhareva, E.A. Buylova, G.U. Yarmuhametova, G.K. Aminova, A.K. Mazitova // Journal of Chemistry. — Vol. 2021. https://doi.org/10.1155/2021/5099705.

25 Pellis A. Renewable polymers and plastics: Performance beyond the green / A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi // New Biotechnology — 2021. — Vol. 60. — P. 146–158.

26 Kaboorani A. Tailoring the low-density polyethylene — thermoplastic starch composites using cellulose nanocrystals and compatibilizer / A. Kaboorani, N. Gray, Y. Hamzeh, A. Abdulkhani // Polymer Testing. — 2021. — Vol. 93. — P. 107007. https://doi.org/10.1016/j.polymertesting.2020.107007.

27 Kocaman S. Chemical and plasma surface modification of lignocellulose coconut waste for the preparation of advanced biobased composite materials / S. Kocaman, M. Karaman, M. Gursoy, G. Ahmetli // Carbohydrate Polymers. — 2017. — Vol. 159. — P. 48–57. http://dx.doi.org/doi:10.1016/j.carbpol.2016.12.016.

28 Gerbin E. Tuning the functional properties of lignocellulosic films by controlling the molecular and supramolecular structure of lignin / E. Gerbin, G.N. Rivière, L. Foulon, Y.M. Frapart, B. Cottyn, M. Pernes, et al. // International Journal of Biological Macro-molecules. — 2021. — Vol. 181. — P. 136–149. https://doi.org/10.1016/j.ijbiomac.2021.03.081.

29 Gaudio I. Water sorption and diffusion in cellulose acetate: The effect of plasticisers / I. Gaudio, E. Hunter-Sellars, I.P. Parkin, D. Williams, S.D. Ros, K. Curran // Carbohydrate Polymers. — 2021. — Vol. 267. — P. 118185. https://doi.org/10.1016/j.carbohol.2021.118185.

30 Bazunova M. The Surface Structure Of Polymer Composites Based On Recycled Polypropylene And Natural Components Of Vegetable Origin In The Process Of Biodegradation / M. Bazunova, R. Salikhov, A. Sadritdinov, V. Chernova, V. Zakharov // J. Pharm. Sci. & Res. — 2018. — Vol. 10, No. 2. — P. 288–292.

31 Yadav N. Degradable or not? Cellulose acetate as a model for complicated interplay between structure, environment and degradation / N. Yadav, M. Hakkarainen // Chemosphere. — 2021. — Vol. 265. — P. 128731. https://doi.org/10.1016/j.chemosphere.2020.128731.

В.В. Глухих, А.Е. Шкуро, П.С. Кривоногов

Лигноцеллюлозалық толтырғыштары бар полимерлі композиттердің биодеградация жылдамдығына және физикалық-механикалық қасиеттеріне компоненттердің химиялық құрамының әсерін қарастыру

Термопластикалық полимер фазасы мен лигноцеллюлозалық толтырғыштармен (TPLC) композитті ғылыми зерттеулердің нәтижелері, оларды дайындау мен қолданудың практикалық тәжірибесі 2016 ж. «Жаңартылатын материалдардан жасалған композиттердің анықтамасының» (2017, John Wiley & Sons, Inc.) сегіз томдығында ұсынылған. Мақалада лигноцеллюлоза толтырғыштары бар полимерлі композиттердің биоыдырау жылдамдығын және физикалық-механикалық қасиеттерін бағалау үшін 2017-2020 жылдар мен 2021 жылдың бірінші жартыжылдығына арналған кітаптар мен мақалаларға талдау жасалған. ТРLС алу мен қолданудың экологиялық және экономикалық болашағы зор, өйткені оларды өндіру үшін ормандардың, ауыл шаруашылық және мұнай шикізатынан алынған полимерлердің қалдықтары пайдаланылуы мүмкін. TPLC қолдану аймағына байланысты олардың биодеградация жылдамдығына қарама-қарсы талаптар бар. Құрылыста және медицинада қолдану үшін материалдар мен бұйымдардың биологиялық ыдырауының минималды жылдамдығы болуы керек. Бір рет колданылатын каптамаға арналған материалдар мен бұйымдар биологиялық ыдырауға бейімді болуы және топырақта, суда, компост ортасында белгілі жылдамдықта биологиялық ыдырауға ұшырай алуы қажет. Зерттеу нәтижелері ТРLС қасиеттеріне физикалық ғана емес, сонымен қатар осы композиттердің барлық компоненттерінің химиялық құрылымы да қатты әсер ететінін көрсетеді. Полимерлердің, толтырғыштардың, әртүрлі мақсаттағы қоспалардың химиялық қасиеттері олардың өнеркәсіптік өндірісінің тиімділігіне әсер етуі мүмкін.

Кілт сөздер: композит, химиялық құрылымы, термопластикалық полимер, толтырғыш, целлюлоза, лигнин.

В.В. Глухих, А.Е. Шкуро, П.С. Кривоногов

Обзор влияния химического состава компонентов на скорость биоразложения и физико-механические свойства полимерных композитов с лигноцеллюлозными наполнителями

Результаты научных исследований композитов с термопластичной полимерной фазой и лигноцеллюлозными наполнителями (TPLC), практический опыт их получения и применения по состоянию на 2016 г. представлены в восьми томах «Handbook of Composites from Renewable Materials» (2017, John Wiley & Sons, Inc.). В статье приведён обзор книг и статей за период 2017-2020 годы и первую половину 2021 г. по оценке скорости биоразложения и физико-механических свойств полимерных композитов с лигноцеллюлозными наполнителями. Получение и применение TPLC имеют большие экологические и экономические перспективы, так как для их производства могут быть использованы отходы биомассы леса, сельского хозяйства и полимеров, получаемых из нефтяного сырья. В зависимости от области применения ТРLС, существуют противоположные требования к скорости их биоразложения. Для применения в строительстве и медицине материалы и изделия должны иметь минимальную скорость биоразложения. Материалы и изделия для одноразовой упаковки должны обладать необходимым потенциалом биоразложения и иметь заданную скорость биоразложения в грунте, воде, компостной среде. Результаты исследований показывают, что на свойства TPLC большое влияние может оказывать, не только физическое, но и химическое строение всех компонентов этих композитов. Химические свойства полимеров, наполнителей, добавок различного назначения могут повлиять на экономичность их промышленного производства.

Ключевые слова: композит, химическая структура, термопластичный полимер, наполнитель, целлюлоза, лигнин.

References

1 Nassar, M.M.A., Alzebdeh, K.I., Perve, Z.T., Al-Hinai, N., & Munam, A. (2021). Progress and challenges in sustainability, compatibility, and production of eco-composites: A state-of-art review. *J Appl. Polym. Sci.*, 51284. https://doi.org/10.1002/app.51284.

2 Vinod, A., Sanjay, M.R., Suchart, S., Jyotishkumar, P. (2020). Review. Renewable and sustainable biobased materials: An assessment on biofibers, biofilms, biopolymers and biocomposites. *Journal of Cleaner Production*, 258, 1-27. https://doi.org/10.1016/j.jclepro.2020.120978.

3 Rodriguez, L.J., Peças, P., Carvalho, H., & Orrego, C.E. (2020). A literature review on life cycle tools fostering holistic sustainability assessment: An application in biocomposite materials. *Journal of Environmental Management*, 262, 110308. https://doi.org/10.1016/j.jenvman.2020.110308.

4 Feng, J., Li, S., Peng, R., Sun, T., Xie, X., & Shi, Q. (2020). Effects of fungal decay on properties of mechanical, chemical, and water absorption of wood plastic composites. *J. Appl. Polym. Sci.*, 50022. https://doi.org/10.1002/app.50022.

5 Matlin, S.A., Mehta, G., Hopf, H., Krief, A., Keßlerf, L., & Kümmerer, K. (2020). Material circularity and the role of the chemical sciences as a key enabler of a sustainable post-trash age Sustainable. *Chemistry and Pharmacy*, *17*, 100312. https://doi.org/10.1016/j.scp.2020.100312.

6 Braghiroli, F.L., Passarini, L. (2020). Valorization of Biomass Residues from Forest Operations and Wood Manufacturing Presents a Wide Range of Sustainable and Innovative Possibilities. *Current Forestry Reports*, 6, 172–183. https://doi.org/10.1007/s40725-020-00112-9.

7 Tajeddin, B., & Momen, R.F. (2020). The effect of wheat straw bleaching on some mechanical properties of wheat straw/LDPE biocomposites. *Journal of Food and Bioprocess Engineering*, *3*, *1*, 23–28. https://doi.org/10.22059/JFABE.2020.75620.

8 Klyosov, A.A. (2010). Drevesno-polimernye kompozity [Wood-plastic composites]. Saint Petersburg: Scientific foundations and technologies [in Russian].

9 Feng, J., Chen, J., Chen, M., Su, X., & Shi, Q. (2017). Effects of biocide treatments on durability of wood and bamboo/high density polyethylene composites against algal and fungal decay. *J. Appl. Polym. Sci.*, 45148. https://doi.org/10.1002/APP.45148.

10 Glukhikh, V.V., Buryndin, V.G., Artemov, A.V., Savinovskih, A.V., Krivonogov, P.S., & Krivonogova, A.S. (2020). Plastics: physical-and-mechanical properties and biode-gradable potential. *Foods and Raw Material*, *8*, *1*, 149–154. https://doi.org/10.21603/2308-4057-2020-1-149-154.

11 Candelier, K., Atli, A., Alteyrac, J. (2019). Termite and decay resistance of bioplast-spruce green wood-plastic composites. *European Journal of Wood and Wood Products*, 77, 157–169. https://doi.org/10.1007/s00107-018-1368-y.

12 Popov, A.A., Zykova, A.K., & Mastalygina, A.K. (2020). Biorazlagaemye kompozitsionnye materialy. (Obzor) [Biodegradable composite materials (Review)]. *Khimicheskaia fizika — Chemical Physics, 39, 6*, 71–80 [in Russian].

13 Polman, E.M.N., Gruter, G.-J.M., Parsons, J.R., & Tietema, A. (2021). Comparison of the aerobic biodegradation of biopolymers and the corresponding bio-plastics: A review. *Science of the Total Environment*, 753, 141953. https://doi.org/10.1016/j.scitotenv.2020.141953 0048-9697.

14 Marczak, D., Lejcus, K., & Misiewicz, J. (2020). Characteristics of biodegradable textiles used in environmental engineering: A comprehensive review. *Journal of Cleaner Production*, 268, 122129. https://doi.org/10.1016/j.jclepro.2020.122129.

15 Fujisawa, S., Saito, T., & Isogai, A. (2018). All-Cellulose (Cellulose–Cellulose) Green Composites. Advanced Green Composites, 111–134. https://doi.org/10.1002/9781119323327.

16 Li, H., Lianga, Y., Li, P., & He, C. (2020). Conversion of biomass lignin to high-value polyurethane: A review. *Journal of Bioresources and Bioproducts*, 5, 3, 163–179.

17 Parvathy, G., AS, S., Jayan, J.S., Raman, A., & Saritha, A. (2021). Lignin based nano-composites: Synthesis and applications. *Process Safety and Environmental Protection*, *145*, 395–410. https://doi.org/10.1016/j.psep.2020.11.017 0957-5820.

18 Gama, N., Ferreira, A., & Evtuguin, D.V. (2021). New poly(lactic acid) composites produced from coffee beverage wastes. *J. Appl. Polym. Sci.*, *138*, *35*, 51434. https://doi.org/10.1002/app.51434.

19 Wolski, K., Cichosz, S., & Masek, A. (2019). Surface hydrophobisation of lignocellulosic waste for the preparation of biothermoelastoplastic composites. *European Polymer Journal*, 118, 481–491.

20 Ninomiya, K., Abe, M., Tsukegi, T., Kuroda, K., Omichi, M., & Takada, K., et al. (2017). Ionic liquid pretreatment of bagasse improves mechanical property of bagasse/polypropylene composites. *Industrial Crops & Products*, 109, 158–162. https://dx.doi.Org/10.1016/j.indcrop.2017.08.019.

21 Shulga, G., Neiberte, B., Jaunslavietis, J., Verovkins, A., Vitolina, S., & Shakels V., et al. (2021). Lignin-containing Adhesion Enhancer for Wood-plastic Composites. *BioResources*, *16*, *2*, 2804–2823. https://10.15376/biores.16.2.2804-2823.

22 Liu, R., Liu, M., Cao, J., Ma, E., Huang, A. (2017). Fungi Resistance of Organo-Montmorillonite Modified Lignocellulosic Flour/Polypropylene Composites. *POLYMER COMPOSITES-2017*. https://doi.org/10.1002/pc.24413.

23 Lukanina, Y.K. & Popov, A.A. (2021). Okso-biodegradiruemye polimernye materialy. (Obzor) [Oxo-biodegradable polymer materials (Review)]. *All materials. An encyclopedic reference book, 6*, 9–15 [in Russian].

24 Vikhareva, I.N., Buylova, E.A., Yarmuhametova, G.U., Aminova, G.K., & Mazitova, A.K. (2021). An Overview of the Main Trends in the Creation of Biodegradable Polymer Materials. *Journal of Chemistry*, 2021. https://doi.org/10.1155/2021/5099705.

25 Pellis, A., Malinconico, M., Guarneri, A., Gardossi, L. (2021). Renewable polymers and plastics: Performance beyond the green. *New Biotechnology*, 60, 146–158.

26 Kaboorani, A., Gray, N., Hamzeh, Y., & Abdulkhani, A. (2021). Tailoring the low-density polyethylene — thermoplastic starch composites using cellulose nanocrystals and compatibilizer. *Polymer Testing*, 93, 107007. https://doi.org/10.1016/j.polymertesting.2020.107007.

27 Kocaman, S., Karaman, M., Gursoy, M., & Ahmetli, G. (2017). Chemical and plasma surface modification of lignocellulose coconut waste for the preparation of advanced biobased composite materials. *Carbohydrate Polymers*, *159*, 48–57. http://dx.doi.org/doi:10.1016/j.carbpol.2016.12.016.

28 Gerbin, E., Rivière, G.N., Foulon, L., Frapart, Y.M., Cottyn B., & Pernes, M. et al. (2021). Tuning the functional properties of lignocellulosic films by controlling the molecular and supramolecular structure of lignin. *International Journal of Biological Macro-molecules*, *181*, 136–149. https://doi.org/10.1016/j.ijbiomac.2021.03.081.

29 Gaudio, I., Hunter-Sellars, E., Parkin, I.P., Williams, D., Ros, S.D., & Curran, K. (2021). Water sorption and diffusion in cellulose acetate: The effect of plasticisers. *Carbohydrate Polymers*, 267, 118185. https://doi.org/10.1016/j.carbpol.2021.118185.

30 Bazunova, M., Salikhov, R., Sadritdinov, A., Chernova, V., & Zakharov, V. (2018). The Surface Structure Of Polymer Composites Based On Recycled Polypropylene And Natural Components Of Vegetable Origin In The Process Of Biodegradation. J. Pharm. Sci. & Res., 10, 2, 288–292.

31 Yadav, N., & Hakkarainen, M. (2021). Degradable or not? Cellulose acetate as a model for complicated interplay between structure, environment and degradation. *Chemosphere*, 265, 128731. https://doi.org/10.1016/j.chemosphere.2020.128731.

Information about authors:

Glukhikh Victor Vladimirovich (corresponding author) — Doctor of technical sciences, Professor, Ural State Forest Engineering University, Siberian tract, 37, 620100, Yekaterinburg, Sverdlovsk region, Russia; e-mail: gluhihvv@m.usfeu.ru; https://orcid.org/0000-0001-6120-1867;

Shkyro Alekseiy Yevgenyevich — Candidate of technical sciences, Docent, Ural State Forest Engineering University, Siberian tract, 37, 620100, Yekaterinburg, Sverdlovsk region, Russia; e-mail: shkuroae@m.usfeu.ru; https://orcid.org/0000-0002-0469-2601;

Krivonogov Pavel Sergeevich — Candidate of technical sciences, Docent, Ural State Forest Engineering University, Siberian tract, 37, 620100, Yekaterinburg, Sverdlovsk region, Russia; e-mail: krivo-nogovps@m.usfeu.ru; https://orcid.org/0000-0001-5171-4482.